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⑤④ Electron beam curable pigmented acrylated polyurethanes.

⑤⑦ Acrylated polyurethane containing 0.1 to 5 or more parts
of pigment can be cured with 0.1 to 5 megarads of electron
beam radiation to give a cured pigment polyurethane having
satisfactory physical properties.

EP 0 107 608 A1

ELECTRON BEAM CURABLE
PIGMENTED ACRYLATED POLYURETHANES

Technical Field

5 This invention relates to an electron beam curable
pigmented acrylated polyurethane composed essentially
of 100 parts of an acrylated polyurethane and at least
about 0.1 and 5 or more parts of pigment and a method
of curing the same by radiating said pigmented
10 polyurethane with 0.1 to 15 megarads of radiation from
an electron beam source.

Background

15 Photocurable polyurethanes have been used in
making photographic plates, sight shields and related
articles. These articles have been essentially
unpigmented and consequently the ability of pigments to
protect and improve the physical properties of the
cured polyurethanes as well as to improve the aesthetic
20 effect has not been used.

Disclosure and Practice of the Invention

 We have discovered that acrylated polyurethane
composed essentially of 100 parts of acrylated
25 polyurethane and at least 0.1 and 5 or more parts of
pigment forms an electron beam curable composition at a
radiation level of 0.1 to 15 megarads which gives cured
compositions having improved physical properties and
especially improved aesthetic values.

30 The acrylated polyurethanes can be prepared by use
of an acrylate diluent or an acrylate reactant to
incorporate the acrylate in the polyurethane.

 Examples of acrylate reactants are the hydroxy and
amino groups containing acrylates. Representative
35 examples of these are the hydroxyl alkyl acrylates or

hydroxyl methacrylates where the alkyl groups preferably have 2 to about 12 carbon atoms such as the ethyl, propyl and butyl radicals. The amino analogs of these hydroxyl alkyl acrylates and methacrylates can be
5 used also but do not yield generally as stable a material.

The acrylate diluents are represented by the acrylates that can function as a plasticizer or diluent for the polyurethanes. Representative of these are the
10 esters of the acrylic and methacrylic acids or their anhydrides with a hydroxy compound such as the representative mono alcohols, the diols and triols. The acrylic and methacrylic esters where the alkyl radical is methyl, ethyl, propyl and higher can be
15 dissolved or dispersed in the polyurethane to acrylate the polyurethane composition.

Particularly desirable are the acrylate diluents produced by reacting an acrylic acid or methacrylic acid or their anhydrides with a polyol such as the
20 glycols or ether glycols of 2 to about 12 carbon atoms. Also the acrylate diluent can be added to the polyurethane reactants before or during their reaction to produce a polyurethane having acrylate in the composition. Alternatively the acrylate reactants can
25 be used to react with the organic polyisocyanate to give a built-in acrylate in the polyurethane composition when the unreacted organic polyisocyanate is reacted with the polyol and/or curative to produce the polyurethane.

30 The nature of this invention may be more readily understood and appreciated by reference to the following representative examples wherein all parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1Preparation of Prepolymer

5 Into a 2000 ml glass resin vessel were added 1000
grams of about 3000 molecular weight polycaprolactone
diol with a reactive number of 39.2. A heating mantle
and a resin kettle top with stirrer, thermometer and
degassing attachments were fitted to the resin pot.
10 With stirring the temperature was raised to 82°C. The
resin was degassed for 30 minutes. Next, the
temperature was raised to 100°C. and 156 grams of
isophorone-diisocyanates were added to the degassed
material which produced a mixture with the ratio of one
15 mole of polyol for two moles of diisocyanate. With
continued stirring the temperature of the materials was
raised to 110°C. To allow for complete reaction, the
mixture was stirred at this temperature for 45 minutes.
The resulting urethane prepolymer was then degassed.
The % free NCO was found to be 2.51.

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Acrylating the Prepolymer

The prepolymer in the resin kettle was cooled to
72°C. To this material was added 94% pure
2-hydroxyethylmethacrylate (HEMA) in the ratio of 1.04
25 equivalents of acrylate to 1.00 equivalents of
isocyanate which worked out to be 8.6 grams of HEMA per
100 grams of prepolymer. Next 2.56 grams of a tin
catalyst was added. With continued stirring, the
temperature of the reaction slowly climbed to 81°C.
30 The mixture was then cooled slowly for 45 minutes until
the temperature dropped to 66°C. The resin kettle top
(along with its attachments) was removed. The bottom
vessel was covered with aluminum foil and left to set
overnight at room temperature.

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Eighteen hours later on the following day a % free NCO analysis of the product was taken and found to be at a value of 0.07. With stirring the contents of the kettle was heated to 72°C. (registered by a thermometer) and 9 grams of butanol were added to get rid of the remaining NCO groups. The warm acrylated prepolymer was then poured into a clear quart jar.

Preparation of pigmented masterbatch

10 In an 800 ml glass beaker were poured 200 grams of the acrylated prepolymer. The contents were heated to 70°C. and 0.4 gram of hydroquinone was added. After heating another ten minutes at 70°C., 33 grams of PDI epoxy 2100 (60% TiO_2 , 40%) was added to the mix with
15 stirring. The pigmented batch was then heated to 82°C. and degassed. Final composition: 100 parts clear acrylated urethane, 10 parts TiO_2 , 6.5 parts epoxy resin.

Radiation Curing

20 Into a 15" x 6" x .020" TeflonTM coated aluminum cavity was poured 50 grams of the warmed masterbatch. A draw down bar was used to take away the excess. The plate with the liquid laden cavity was placed on a
25 conveyor belt and made to pass under the electron beam (taking less than one second) giving the urethane 1.1 megarads of radiation. A second pass under the beam gave the material 1.1 megarads of radiation more for a total dosage of 2.2 megarads.

30 Since there was a slight tackiness to the surface of the urethane, it was dusted with talc. The film could then be stripped from the TeflonTM. It was flexible, rubbery and possessed good strength.

Physicals

Tensile	680 psi
Ultimate Elongation	120%
100% modulus	520 psi

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Preparation of Prepolymer

Same procedure was followed as for Example #1.
Analysis of prepolymer was 2.47% free NCO this time.

10 Acrylating the Prepolymer

Same description as before except substitute 94% pure HEA (2-hydroxyethylacrylate) for HEMA. Used 7.6 g HEA per 100 grams prepolymer. Final % free NCO of acrylated prepolymer was 0.09 which was "killed" with 10 grams of butanol.

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Preparation of Pigmented Masterbatch

Same as for Example #1

20 Radiation Curing

Same procedure as for Example #1 except that the material was cycled twice under the electron beam at 1.0 megarads per cycle which gave a total radiation dosage to the urethane of 2.0 megarads.

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Physicals

Tensile	740 psi
Ultimate Elongation	120%
100% Modulus	500 psi

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EXAMPLE 2

A prepolymer was prepared by reacting 2 moles of isophrone diisocyanate with a mole of polycaprolactone diol of 3000 molecular weight and then reacted with

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1.04 moles of HEMA to cap the prepolymer. This capped prepolymer was used to form a pigmented prepolymer by adding and mixing therein to each 100 parts of capped prepolymer 16 parts of a blend of 10 parts of titanium dioxide and 6 parts of epoxy resin 828, a trade designation of a resin formed by reacting bis phenol A with epichlorohydrin. This blend of pigment and polyurethane was labeled blend A. Other pigmented polyurethanes were made by using other hydroxylalkyl acrylate or methacrylate to cap the prepolymer of this example by replacing the HEMA with respectively hydroxyl propyl acrylate (HPA) and hydroxylethyl acrylate (HEA) in the preparation of the polyurethanes and then adding 16 parts of epoxy resin-titanium-resin to give a white pigmented polyurethane.

The pigmented blend made with HPA containing polyurethane was labeled Blend B and the one made with the HEA containing blend was labeled Blend C. A hundred parts of each of the blends, A, B and C, respectively, was mixed with 1 part of a trifunctional isocyanate, a crosslinker, designated by the tradename Desmodur-N by Mobay Chemical Company. These blends were labeled A-N, B-N and C-N respectively to indicate that Blends A, B and C now contained Desmodur-N. To 100 parts aliquot of each of Blends A-N, B-N and C-N 25 parts of powdery silicon dioxide was added and incorporated. Also, 5 parts of trimethylol propane triacrylate, was added to another 100 parts aliquot of Blends A-N, B-N and C-N, respectively. Then aliquots of each of the blends, A, B and C and blends A-N, B-N and C-N alone or containing 25 parts of silicon dioxide and 5 parts of the crosslinking promoter, trimethylol propane triacrylate were subjected to radiation from an electron beam source at rates of 1 megarads and higher to cure the aliquots. The blends containing the

crosslinking promoter cured faster. All the cured samples had good tensile and flex properties as well as cold cracking and weather resistance.

5 Tires were painted with the curable white pigmented polyurethane composition of these examples to give a white side wall strip to the tire. Then the white sidewall strip was subjected to 5 megarads of electron beam radiation to cure the composition to yield a white side tire. The strip had good adhesive
10 and flex life. Also, these curable pigmented polyurethane compositions were used to form belts, preferably thin and as belt covers for regular rubber belts.

15 This invention has been described and exemplified with electron beams although it should be appreciated any high energy radiation can be used, with the term high energy radiation being used to include electron beams, x-rays and gamma rays.

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CLAIMS

1. A high energy radiation curable pigmented
acrylated polyurethane composition composed essentially
of 100 parts of an acrylated polyurethane and 0.1 to 40
10 parts of a pigment.

2. A method of curing a pigmented acrylated
polyurethane composition containing essentially 0.1 to
40 parts of pigment per 100 parts comprising radiating
15 said composition with 0.1 to 15 megarads from a high
energy radiation source.

3. The method of curing a pigmented acrylated
polyurethane compound of Claim 2 wherein the high
20 energy radiation source is an electron beam.

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European Patent
Office

EUROPEAN SEARCH REPORT

0107608

Application number

EP 83 63 0154

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	US-A-3 989 609 (K. BRACK) * Column 19, claim 1; column 2, lines 11-24, 35-42; column 4, lines 5-28 *	1-3	C 09 D 3/72 C 08 L 75/04 C 08 K 3/22 C 08 F 299/06 C 08 G 18/67 B 60 C 13/00
X	GB-A-1 147 732 (THE O'BRIEN CORP.) * Pages 4,5; claims 1,2,10,11; page 1, lines 40-80; page 2, lines 62-84; page 3, lines 91-106 *	1-3	
X	DE-A-1 916 500 (WEYERHAEUSER) * Pages 13-15, claims 1,2,7,12; page 7, paragraph 3; page 9, paragraph 2 *	1-3	
X	CHEMICAL ABSTRACTS, vol. 84, no. 8, 23rd February 1976, page 122, no. 46282f, Columbus, Ohio, US & JP - A - 75 111 191 (MITSUBISHI RAYON CO., LTD.) 01-09-1975	1-3	TECHNICAL FIELDS SEARCHED (Int. Cl. 3) C 09 D C 08 L C 08 F C 08 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 02-01-1984	Examiner VAN PUymbROECK M.A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			